8.1   System Processes

The design of a fuel cell system involves more than the optimizing of the fuel cell section with respect to efficiency or economics. It involves minimizing the cost of electricity (or heat and electric products as in a cogeneration system) within the constraints of the desired application. For most applications, this requires that the fundamental processes be integrated into an efficient plant with low capital cost. Often these objectives are conflicting, so compromises, or design decisions, must be made. In addition, project-specific objectives, such as desired fuel, emission levels, potential uses of rejected heat (electricity, steam, or heat), desired output levels, volume or weight criteria (volume/kW or weight/kW), and tolerance for risk all influence the design of the fuel cell power system.

8.1.1   Fuel Processing

Fuel processing is defined in this Handbook as the conversion of a commercially available gas, liquid, or solid fuel to a fuel gas reformate suitable for the fuel cell anode reaction. Fuel processing encompasses the cleaning and removal of harmful species in the fuel, the conversion of the fuel to the fuel gas reformate, and downstream processing to alter the fuel gas reformate according to specific fuel cell requirements. Examples of these processes are:

- Fuel Cleaning – Removal of sulfur, halides, and ammonia to prevent fuel processor and fuel cell catalyst degradation.
- Fuel Conversion – Converting a fuel (primarily hydrocarbons) to a hydrogen-rich gas reformate.
- Reformate Gas Alteration – Converting carbon monoxide (CO) and water (H_2O) in the fuel gas reformate to hydrogen (H_2) and carbon dioxide (CO_2) via the water-gas shift reaction; selective oxidation to reduce CO to a few ppm, or removal of water by condensing to increase the H_2 concentration.

A fuel processor is an integrated unit consisting of one or more of the above processes, as needed for the fuel cell requirements[41] and the fuel, that function together to be cost effective for the application. Design considerations may include high thermal efficiency, high hydrogen yield (for some fuel cells hydrogen plus carbon monoxide yield), multi-cycling, compactness, low weight, and quick starting capability, depending on the application.

Figure 8-2 depicts the Processing steps needed for a low temperature cell.[42] Most fuel processors make use of the chemical and heat energy left in the fuel cell effluent to provide heat for fuel processing thus enhancing system efficiency.

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41.   Primarily determined by the cell's operating temperature.
42.   Requires relatively complex fuel processing.

Figure 8-2 Representative Fuel Processing Steps & Temperatures
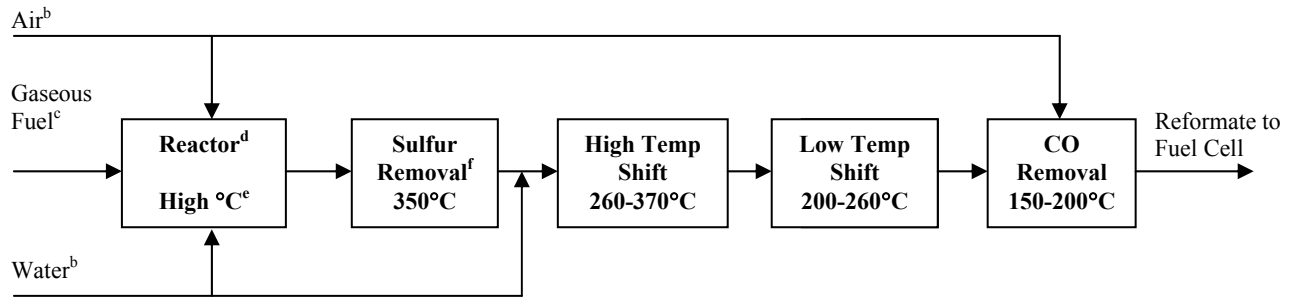
a) - For MCFC & SOFC, no high temperature shift, low temperature shift, or CO removal required.
   - For PAFC and circulating AFC, no CO removal required after low temperature shift.
   - For PEFC, all components required except that for high temperature CO removal eliminated or reduced in complexity.
b) Possible to use residual air, water, and heat of fuel effluent from fuel cell and other downstream components.
c) Vaporizer required for liquid fuels.
d) Non-catalytic POX fuel processor does not require water.
e) Temperature dependent on fuel, sulfur content of fuel, and type of reactor.
f) Can be located prior to, within, or after the reactor; liquid desulfurizer located prior to the vaporizer.

Fuel conversion and alteration catalysts are normally susceptible to deactivation by impurities,[43] thus the fuel cleaning process takes place upstream or within the fuel conversion process. The fuel conversion and reformate gas alteration processes can take place either external to the fuel cell or within the fuel cell anode compartment. The former is referred to as an external reforming fuel cell and the latter is referred to as an internal reforming fuel cell. Cells are being developed to directly react commercially available gas and liquid fuels, but the chemically preferred reaction of present fuel cells is via hydrogen-rich gas. This discussion will address external reforming fuel processors only. Descriptions of internal reforming are contained within the specific fuel cell sections. The system calculation section provides examples of heat and material balances for both externally and internally reforming fuel cells.

Fuel processors are being developed to allow a wide range of commercial fuels suitable for stationary, vehicle, and military applications. Technology from large chemical installations has been successfully transferred to small, compact fuel cells to convert pipeline natural gas, the fuel of choice for small stationary power generators. Several hundred multi-kWe commercial fuel cell units are operating that contain fuel processors (see Section 1.6). Cost is an issue, as it is with the entire fuel cell unit, for widespread commercial application. Scaling of existing fuel processing technology to larger fuel cell power plants will reduce the specific cost of the fuel processor.

Natural gas fuel reforming for fuel cells is essentially mature. Recent fuel processor research and development has focused on fuels for transportation and military applications.

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43. Referred to as poisoning in catalysis literature. Ni-based fuel processing catalysts are poisoned by "physiadsorbtion" of S onto the Ni surface, thus reducing performance. Pt catalysts are less susceptible to S poisoning because S does not physiadsorb as strongly as it does on Ni; thus affecting performance less.

The issue with transportation is how to match a plausible commercial fuel infrastructure with the requirements of the fuel cell unit to be competitive. Economics drive the fuel of choice toward existing infrastructure, such as gasoline. Fuel cell requirements drive the fuel toward methanol or a "fuel cell friendly" gasoline. Environmental concerns drive the fuel of choice toward pure hydrogen[44]. Gasoline is a complex fuel, requiring high conversion temperature, and it has high levels of impurities that affect catalytic activity (see Appendix A). Methanol fuel processors (regarded by some as a necessary step towards an eventual liquid transportation fuel) are easier to develop than processors capable of converting gasoline. However, use of methanol or hydrogen would require major changes to the fuel supply infrastructure. Processors for both methanol and gasoline have been tested up to the 50 kWe level for vehicle application. What fuel to use onboard the vehicle is open to question at this time, but recent research in the fuel cell community points toward a modified gasoline tailored for fuel cell use that could be supplied through the existing fuel infrastructure (1).

The U.S. military has a substantial fuel supply infrastructure in place. The two predominant fuel types in this infrastructure are diesel and jet fuel, a kerosene. It is highly improbable that the U.S. military would change these fuels to accommodate fuel cells. Use of a fuel more suitable to the fuel cell would limit the technology's military use (there is R&D activity for fuel cell power packs to provide man-portable soldier power using hydrogen cartridges, or other hydrogen-containing forms, as well as methanol). Diesel and jet fuel are two of the most difficult conventional fuels to convert to a hydrogen-rich gas. They contain large amounts of sulfur that deactivate catalysts and require high conversion temperature. Fuel processors that convert diesel and jet fuel to a hydrogen-rich gas are in the early stages of development. The technology has been demonstrated at a 500 W size; 50 kWe units are being developed. Argonne National Laboratory (ANL) has operated a 3 kWe autothermal reformer with direct injection of diesel-like hydrocarbons – hexadecane and dodecane. Experiments with real diesel are anticipated shortly (2).

Fuel Processing Issues

Major issues that influence the development of a fuel processor are 1) choice of commercially available fuels suitable for specific applications; 2) fuel flexibility; 3) catalyst tolerance; 4) fuel cell size, and 5) vaporization of heavy hydrocarbons. Heavy hydrocarbons, such as diesel, require vaporization temperatures much in excess of 350-400°C, at which temperature some of the heavier fuels pyrolyze.

Fuel Choice and Flexibility: The fuel cell is a power generation technology that is in the early stages of commercial use. As a result, it is paramount to target applications that have the potential for widespread use (to attract adequate financial investment) with the simplest technology development (to minimize development cost). There is a strong relation between viable applications and the infrastructure of available fuels.

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44. The US FreedomCAR program is focused primarily towards hydrogen and secondarily towards "gasoline" as the onboard fuel.

High-value niche markets drove early fuel cell technology development. These included the use of fuel cells for on-board electric power in space vehicles, and to demonstrate that fuel cells are an efficient, environmentally-friendly technology for stationary on-site commercial power.

The technology of choice for on-board electric power on mid-length space vehicle missions (several days to a year), including the important man-moon mission, was the fuel cell. This was because the use of batteries for more than a couple of days proved too heavy, combustion engines and gas turbines required too heavy a fuel supply, and the use of a nuclear reactor was only suitable for missions of a year or more. There was a simple choice of fuel for space fuel cells: it was hydrogen because it doesn't require a fuel processor other than storage and pressurization, it is relatively lightweight when stored under pressure, and it was the best fuel for the early-developed alkaline fuel cell. Fuel flexibility was not an issue.

It was logical to exploit fuel cell space development for terrestrial use. The initial terrestrial application was to increase power generation efficiency (in reaction to the oil crisis of the early 1970s) and to improve the environment by lowering fossil-fueled power generation exhaust emission. Although coal-derived gas was recognized as a viable fuel, early fuel cell development was based on conveniently accessible pipeline gas prior to turing attention to coal-derived gas. One of the major fuel cell sponsors at the time was the natural gas industry.

Pipeline gas consists primarily of methane that is relatively easy to purify. The technology to convert methane to a H_2-rich gas existed for large chemical plants. Developers had only to adapt existing technology to small fuel cell units, not easy due to several magnitudes of scale-down. Owners of stationary power plants usually desire fuel flexibility. Fortunately, the fuel processor on these early plants could convert a light distillate, such as naphtha, with minor changes (e.g., add a vaporizer, change-out the fuel nozzles).

Once the niche markets were exploited to start fuel cells on their development path, it became necessary to target widespread potential applications while keeping technology development as simple as possible. General application areas of present interest to the fuel cell community are multi-kWe residential, commercial, and light industrial stationary power, transportation prime and auxiliary power, and military uses.

In summary, these are the applications and coupled fuel choices of interest to fuel cell technology to date:

- H_2 is preferable for a closed environment such as space vehicle application. There are sources of H_2-rich gases, such as an off-gas at a chemical plant, that require only fuel cleaning. Fuel flexibility is not applicable in either case.
- The fuel choice for small, stationary power plants is pipeline gas due to its availability for multiple commercial, light-industrial, and residential applications. Some users request that the fuel processor convert at least one additional fuel, i.e., a light distillate.
- Light vehicles is a key commercial target due to the large number of potential units; the fuel choice is open to question. Some proponents support the use of on-board hydrogen. There is a strong argument for liquid fuels due to on-board volume restrictions and existing fuel supply infrastructure. Candidate liquid fuels for light vehicles could be available gasoline or

a new gasoline, if driven by the infrastructure. Methanol may have an edge if it proves too difficult to process gasoline, provided the use of methanol compares favorably on a cost and environmental basis with present internal combustion engine (ICE) gasoline. Fuel flexibility in processors should be considered because of the indecision on fuel type and because the public is accustomed to a selection of different octane liquid fuels and diesel.

- The present infrastructure fuel for heavy vehicles is high sulfur diesel (now ~500 ppm sulfur by weight) but this may change to a nearly sulfur-free diesel as proposed by the EPA. Beginning June 1, 2006, refiners must produce a diesel containing a maximum of 15 ppm sulfur (3). The fuel for this sector could also be a gasoline if such a fuel cell system could compete.
- On-board vehicle auxiliary power is increasing dramatically to satisfy consumer convenience demands. Fuel selection for these applications parallel light and heavy vehicle fuels.
- The military will continue with its fuel infrastructure of high sulfur diesel (up to 1,000 ppm sulfur by weight) and jet fuel (JP-8, up to 300 ppm by weight). Sulfur specification will remain high because the military has to consider worldwide fuel sources. High sulfur diesel and JP-8 are close in characteristics, so no fuel flexibility is required. However, there is a possibility that some parts of the military or the Coast Guard (a military service within the DOT) could use fuels more compatible to the fuel cell in limited applications.
- As environmental regulation becomes more stringent for megawatt-size power stations and fuel cells are scaled larger in size, there is the possibility to use the U.S.'s most plentiful, indigenous fuel, coal. The term, coal, covers a broad spectrum of solid fuels that complicate fuel processing, particularly cleanup.
- There is the possibility of using other available fuels such as light distillates, ethanol, anaerobic digester gas, biomass, and refuse-derived fuel.

The market that has the greatest impact on fuel processor development at this time is in the light vehicle application sector, due to the potential large number of units. Some fuel processor developers are focusing on the development of methanol fuel processing either as the fuel of choice or as a development step toward processing gasoline. Others consider that it is best to develop a vehicle that uses the most environmentally attractive fuel, hydrogen. There are numerous opinions reagarding fuel and infrastructure best-suited for the light vehicle transportation market.

Methanol is unquestionably the easiest of the potential liquid fuels to convert to hydrogen for vehicle use. Methanol disassociates to carbon monoxide and hydrogen at temperatures below 400°C and can be catalytically steam reformed at 250°C or less. This provides a quick start advantage. Methanol can be converted to hydrogen with efficiencies of >90 %. But methanol is produced primarily from natural gas, requiring energy, and it is less attractive than gasoline on a well-to-wheels efficiency basis (5, 6).

Gasoline has many advantages over methanol, but conversion to H_2 requires temperatures in excess of 650°C and produces greater amounts of CO, methane (CH_4), and possibly coke. Without catalyst, the conversion temperature is 1,000°C or higher. High temperatures require special materials of construction and significant preheating. Petroleum-derived fuels contain more sulfur and trace amounts of metal that could be harmful to the fuel cell. Natural gas is not

good for transportation because of its low relative energy density and 700°C or higher processing temperature (7).

ExxonMobil has presented a position paper (8) for liquid fuels that addresses the pros and cons of methanol versus gasoline. Paraphrased excerpts from this are:
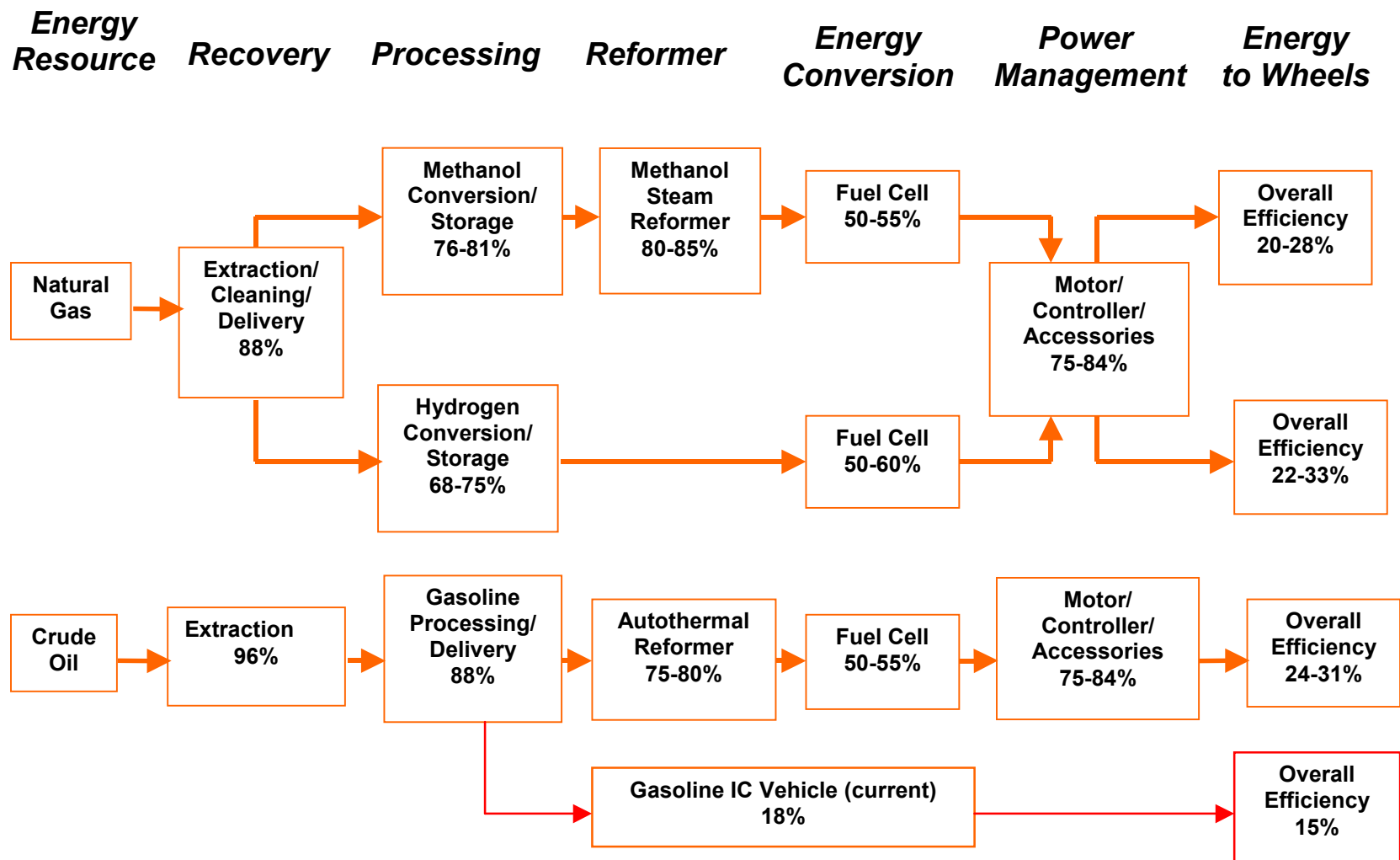
- Fuels that are most directly suited to the fuel cell are the most difficult and costly to produce and distribute. Gasoline and methanol are the leading candidates to power fuel cell engines. Both the gasoline and methanol fuel cell vehicles should be more fully developed prior to making a commercial decision on fuel choice.
- Due to methanol's corrosivity and its affinity for water, it cannot be readily distributed in today's fuel infrastructure. Methanol burns with a nearly invisible flame. Available luminosity additives won't reform in the low-temperature methanol steam reformers. Methanol is more acutely toxic than gasoline. Additives that are likely to be needed for safety and health reasons will impact the fuel processor's performance and cost.
- Gasoline fuel processing has the ability to utilize the existing infrastructure, a major advantage. It is inherently more flexible than the low temperature methanol processor, allowing multiple fuel use in the same system. The gasoline processor is also more tolerant of contaminants or additives contained in the fuel. Due to the higher energy density of gasoline, the gasoline system offers the potential for up to twice the vehicle range of the methanol system. Today's mid-sized passenger cars are about 15 to 18 % "well-to-wheels" energy efficient as indicated in Figure 8-3.[45] Despite the increased vehicle efficiency of a methanol fuel-based system, the resultant "well-to-wheel" efficiency would be only 20 to 28%, lower than either gasoline hybrids or gasoline fuel cell vehicles.
- A customized gasoline for fuel cells could offer better performance and be produced at lower cost because many of conventional gasoline's more expensive ingredients would not be required. Naphtha is a common refinery stream that is an inexpensive alternative to conventional gasoline. Although its octane is too low for today's ICE, naphtha is ideal for fuel cells and could be supplied to retail stations within the existing gasoline infrastructure.

Fuel Cell and Fuel Processor Catalyst Tolerance: There are major fuel requirements for the gas reformates that must be addressed. These requirements result from the effects of sulfur, carbon monoxide, and carbon deposition on the fuel cell catalyst. The activity of catalysts for steam reforming and autothermal reforming can be affected by sulfur poisoning and coke formation; this commonly occurs with most fuels used in fuel cells of present interest. Other fuel constituents can also prove detrimental to various fuel cells. Examples of these are halides, hydrogen chloride, and ammonia.

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45. Editor's note - The gasoline-fueled ICE well-to-wheel efficiency values apply to today's technology and are averaged over the entire driving cycle. Advanced IC engine/vehicles are more efficient over the entire operating cycle than 18 % (up to 20 some odd %). This implies that future IC engine/vehicle efficiency for light vehicles can be in excess of the 15 to 18 % quoted in the ExxonMobil paper. Vehicle miles per gallon increase when the ICE is combined with a battery in developmental vehicles with very low drag coefficients. For example, the 60+ mpg for the Honda Insight, 40 to 50+ mpg for the Toyota Prius, 70+ mpg for the Ford Prodigy, and ~80 mpg for the GM Precept. The overall well-to-wheel efficiency over a standard city/highway driving cycle for a four passenger, production hybrid vehicle has been estimated to be about 25-30 %, close to a fuel cell vehicle. The fuel cell engines for lightweight vehicles are likely to be hybrids, and therefore the projected efficiencies must be carefully considered.

There are discrepancies in the tolerance for harmful species specified by fuel cell developers, even for similar type fuel cells. These discrepancies are probably due to electrode design, microstructure differences, or in the way developers establish tolerance. In some cases, the presence of certain harmful species causes immediate performance deterioration. More often, the degradation occurs over a long period of time, depending on the developer's permissible exposure to the specific harmful species. Here, the developer establishes an estimated cell life based on economics. The permissible amount of the harmful constituent is then determined based on economic return vs. fuel cell life expectancy.

Figure 8-3 "WELL-TO-WHEEL" EFFICIENCY FOR VARIOUS VEHICLE SCENARIOS (9)

Energy Resource	Recovery	Processing	Reformer	Energy Conversion	Power Management	Energy to Wheels
		Methanol Conversion/ Storage 76-81%	Methanol Steam Reformer 80-85%	Fuel Cell 50-55%		Overall Efficiency 20-28%
Natural Gas	Extraction/ Cleaning/ Delivery 88%				Motor/ Controller/ Accessories 75-84%	
		Hydrogen Conversion/ Storage 68-75%		Fuel Cell 50-60%		Overall Efficiency 22-33%
Crude Oil	Extraction 96%	Gasoline Processing/ Delivery 88%	Autothermal Reformer 75-80%	Fuel Cell 50-55%	Motor/ Controller/ Accessories 75-84%	Overall Efficiency 24-31%
			Gasoline IC Vehicle (current) 18%			Overall Efficiency 15%

Sulfur Effects

Present gasolines contain approximately 300 ppm by weight of sulfur. New government standards will reduce the sulfur concentration to an average of 30 ppm and a maximum of 80 ppm by 2006; however fuel gas produced from these gasolines may contain as high as 3-8 ppm of H_2S. No. 2 fuel oil contains 2,200 to 2,600 ppm of sulfur by weight. Even pipeline gas contains sulfur-containing odorants (mercaptans, disulfides, or commercial odorants) for leak detection. Metal catalysts in the fuel reformer can be susceptible to sulfur poisoning, requiring that the sulfur in the fuel reformate be removed. Some researchers have advised limiting the sulfur content of the fuel from a steam reformer to less than 0.1 ppm, but note that the limit may be higher in an autothermal reformer (10).

Sulfur poisons catalytic sites in the fuel cell also. The effect is aggravated when there are nickel or iron-containing components, including catalysts that are sensitive to sulfur and noble metal catalysts such as found in low temperature cell electrodes. Sulfur tolerances are described in the specific fuel cell sections of this handbook.[46] In summary, the sulfur tolerances of the cells of interest, by percent volume in the cleaned and altered fuel reformate gas to the fuel cells from published data, are:

- PEFC - <50 ppm sulfur as H_2S (11), poisoning is cumulative and not reversible.
- PAFC - <50 ppm sulfur as H_2S + COS or <20 ppm sulfur as H_2S at the anode. Poisoned anodes can be re-activated by polarization at high potentials.
- MCFC - <0.5 ppm sulfur as H_2S (at the cathode) equates to <10 ppm at the anode because of fuel exhaust being sent to the cathode in an MCFC (same amount of sulfur, more gas at the cathode), poisoning is reversible.
- SOFC - <1 ppm sulfur as H_2S, poisoning is reversible for the tubular SOFC. H_2S levels of 1 ppm result in an immediate performance drop, but this loss soon stabilizes into a normal linear degradation. Tests show that high temperature planar SOFCs with all-ceramic components can tolerate up to 3,000 ppm of sulfur. Sulfur, in H_2S form, has been used as a fuel for an external reforming, all-ceramic SOFC operating at 1,000°C (12). However, developers want to reduce the cell temperature to allow less expensive metal components, primarily interconnects, and improve cycle efficiency. There is a requirement to lower sulfur significantly if metal parts are used in an SOFC. For planar SOFCs, claims for sulfur tolerance vary among the developers. The range of sulfur has been published as 10 to 35 ppm. Planar SOFC sulfur tolerance probably will be secondary to the fuel processor catalyst that, as mentioned, may be as low as 0.1 ppm.

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46. There is ambiguity in the way sulfur is reported in fuel cell literature that has caused confusion in the amount that can be tolerated. Reports often fail to distinguish whether the sulfur is measured by weight, as it would be before vaporization of a liquid fuel, or by volume, as it would be in a gas fuel or fuel gas reformate. An approximate rule of thumb is that the amount (by volume) of sulfur in a vaporized fuel is one-tenth the amount of sulfur measured by weight in the liquid fuel. 300 ppm sulfur (by weight) in the liquid fuel equates to 30 ppm sulfur (by volume) when the fuel is converted to a gaseous reformate.
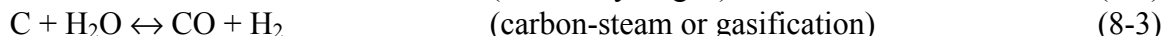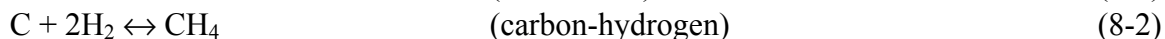
Carbon Monoxide Effects

Carbon monoxide, a fuel in high temperature cells (MCFC and SOFC), is preferentially absorbed on noble metal catalysts that are used in low temperature cells (PAFC and PEFC) in proportion to the H_2:CO partial pressure ratio. A particular level of carbon monoxide yields a stable performance loss. The coverage percentage is a function of temperature, and that is the sole difference between PEFC and PAFC (13). Cell limits are:

- PEFC – Consensus tolerance is <50 ppm into the anode.
- PAFC – Major US manufacturer set tolerance limit as <1.0 % into the anode.
- MCFC – CO and H_2O shift to H_2 and CO_2 in the cell as the H_2 is consumed by the cell reaction due to a favorable temperature and catalyst.
- SOFC – CO can be a fuel. However, if the fuel gas contains H_2O, the shift reaction (CO + $H_2O \rightarrow H_2 + CO_2$) is chemically favored.

Carbon Deposition Effects

The processing of hydrocarbons always has the potential to form coke (soot). If the fuel processor is not properly designed or operated, coking is likely to occur (7). Carbon deposition not only represents a loss of carbon for the reaction, but more importantly results in deactivation of catalysts in the processor and the fuel cell due to deposition at the active sites. Thermodynamic equilibrium provides a first approximation of the potential for coke formation. The governing equations are:

$$C + CO_2 \leftrightarrow 2CO \qquad \text{(Boudouard)} \qquad (8\text{-}1)$$
$$C + 2H_2 \leftrightarrow CH_4 \qquad \text{(carbon-hydrogen)} \qquad (8\text{-}2)$$
$$C + H_2O \leftrightarrow CO + H_2 \qquad \text{(carbon-steam or gasification)} \qquad (8\text{-}3)$$

The possible formation of carbon using a particular fuel can be determined by the simultaneous solution of the above equations using their equilibrium coefficients.[47] No solid graphitic carbon exists at low temperatures (~600°C) in binary mixtures containing at least 2 atoms of oxygen or 4 atoms of hydrogen per atom of carbon (14).

Fuel Cell Unit Size: The size of the fuel cell is a characteristic that impacts fuel processor selection. There is a lower level of power output at which it is no longer advantageous to incorporate a fuel processor. The decision is also application-specific. It is likely that releasing H_2 by chemical reaction from a solid compound when mixed with water is economical for small portable units (below 100 W). An H_2 storage cartridge can be replaced in seconds (15). Actually the power level at which the tradeoff is likely to occur changes as processing and storage technology advances. One fuel processor developer has produced a 100 W partial oxidation (POX) methane reactor the size of a coffee can. The unit includes a reforming zone, shift reactors, and all heat exchangers. H_2 is 36% (assume dry) and the CO level can be reduced to 1%. The unit runs on methane, propane, and ethanol (16). Another research project is investigating methanol reformers for sub-watt fuel cell power sources for the Army.

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47. Carbon is slightly less likely to be deposited than equilibrium coefficient calculations indicate, due to kinetics.

Fuel Processing Techniques

The generic term most often applied to the process of converting liquid or gaseous light hydrocarbon fuels to hydrogen and carbon monoxide is "reforming". There are a number of methods to reform fuel. The three most commercially developed and popular methods are 1) steam reforming, 2) partial-oxidation reforming, and, 3) autothermal reforming.

Steam reforming (SR) provides the highest concentration of hydrogen and can obtain a conversion efficiency. Partial oxidation (POX) is a fast process, good for starting, fast response, and a small reactor size. Non-catalytic POX operates at temperatures of approximately 1,400°C, but adding a catalyst (catalytic POX or CPOX) can reduce this temperature to as low as 870°C. Combining steam reforming closely with CPOX is termed autothermal reforming (ATR).

Steam Reforming: Historically, steam reforming has been the most popular method of converting light hydrocarbons to hydrogen. The fuel is heated and vaporized, then injected with superheated steam into the reaction vessel. The steam-to-carbon molar ratio is usually in the neighborhood of 2.5:1 but developers strive for lower ratios to improve cycle efficiency. Excess steam is used to force the reaction to completion as well as to inhibit soot formation. Like most light hydrocarbons, heavier fuels can be reformed through high temperature reaction with steam. Steam reforming is usually carried out using nickel-based catalysts. Cobalt and noble metals are also active, but more expensive. The catalytic activity depends on metal surface area. For nickel, the crystals sinter quickly above the so-called Tamman temperature (590°C), approaching a maximum size related to the pore diameter of the support. The crystal growth results in loss of surface area and activity (17). The steam reformer can operate with or without a catalyst. Most commercial applications of steam reforming use a catalyst to enhance reaction rates at decreased temperatures. Lower temperatures favor high CO and hydrogen concentration. The reforming catalyst also promotes the water-gas shift reaction. Steam reforming is endothermic, thus favored by high temperatures. But it is a slow reaction and requires a large reactor (4). As a result, rapid start and transients cannot be achieved by steam reforming due to its inherently slower indirect heating (18). Steam reforming suits pipeline gas and light distillate stationary fuel cell power generation well.

The exothermic water-gas shift reaction occurs in the steam reformer reactor. The combined reaction, steam reforming and water gas shift, is endothermic. As such, an indirect high temperature heat source is needed to operate the reactor. This heat source usually takes the form of an adjacent, high-temperature furnace that combusts a small portion of the fuel or the fuel effluent from the fuel cell. Efficiency improves by using rejected heat from other parts of the system. Note that the intrinsic water-gas shift in the reactor may not lower the CO content to the fuel cell requirement, and additional shifting will be needed for lower temperature fuel cells.

Steam reforming of higher hydrocarbons can be used to produce methane suitable for use in high temperature internal reforming fuel cells. Steam pre-reforming of hydrocarbons, as a process step in the manufacture of hydrogen, ammonia, methanol, carbon monoxide, and syngas, is an established technology. All higher hydrocarbons are converted over a nickel-based catalyst into a gas mixture containing hydrogen, methane, and carbon oxides. Establishment of methanation and shift reaction equilibria at the process conditions determines the composition of the pre-

reformed gas. By proper design of fuel processing systems, a wide variety of fuels may be converted to a suitable reformate. This reformate can then be used to promote internal reforming for high temperature fuel cell systems. For each type of fuel, optimum operating parameters such as temperature, steam/carbon ratio, and catalyst must be established (19).

Partial Oxidation: A substoichiometric amount of air or oxygen is used to partially combust the fuel. Partial oxidation is highly exothermic, and raises the reactants to a high temperature. The resulting reaction products, still in a reduced state, are then quenched through the introduction of superheated steam. The addition of steam promotes the combined water-gas shift and steam reforming reactions, which further cools the gas. In most cases, and with sufficient pre-heating of the reactants, the overall reaction is exothermic and self-sustaining. For some applications however, particularly small-scale configurations, a catalyst can be used to increase reaction rates at lower reaction temperatures. As with steam reforming, additional, water-gas shift may be necessary to satisfy the fuel cell requirements.

POX reactor temperatures vary widely. Noncatalytic processes for gasoline reforming require temperatures in excess of 1,000°C. These temperatures require the use of special materials and significant preheating and integration of process streams. The use of a catalyst can substantially reduce the operating temperature, allowing the use of more common construction materials such as steel. Lower temperature conversion leads to less carbon monoxide (an important consideration for low temperature fuel cells), so that the shift reactor can be smaller. Lower temperature conversion will also increase system efficiency.

For some heavy hydrocarbon fuels, typical values range from as low as 870°C for catalytic POX upwards to 1,400°C for non-catalytic POX. For sulfur-bearing diesel fuel, a catalytic POX reactor will usually operate at approximately 925°C. This relatively elevated temperature is needed to overcome catalyst degradation due to the presence of sulfur. Non-catalytic POX reactors operate at around 1,175°C on diesel fuel.

Advantages of POX that make this type of fuel conversion suitable for transportation power are:

- POX does not need indirect heat transfer (across a wall), so the processor is more compact and lightweight (7).
- Contrary to widely-held opinion, POX and ATR are capable of higher reforming efficiencies than are steam reformers (20).

Partial oxidation should be reacted so that the overall reaction is exothermic, but at a low oxygen-to-fuel ratio to favor higher hydrogen yields.

It is a widely-held opinion that POX leads to lower efficiency than steam reforming due to the POX reaction being exothermic. However, a thorough examination of the thermodynamics shows that POX and ATR have higher reforming efficiencies than steam reformers. This raises the question why there is a need to use steam reforming or an ATR if the POX's efficiency is higher. The minimum allowable oxygen to carbon (O/C) ratio is 1 for the POX process. This generates high heat that leads to undesirable high temperatures (low H_2, CO_2 selectivity, materials of construction constraints, etc.). The steam reformer and ATR allow lower O/C ratios, keep the temperature down, and result in higher CO_2 and H_2 selectivity (more H_2 yield per mole of fuel).

Autothermal Reforming: The coupling of SR with POX is termed autothermal reforming (ATR). Some define ATR as a SR reaction and a POX reaction that take place over microscopic distances at the same catalytic site, thus avoiding complex heat exchange (21). Others have the less restrictive definition that ATR occurs when there is no wall between a combined SR reaction and catalytic POX reaction. ATR is carried out in the presence of a catalyst that controls the reaction pathways and thereby determines the relative extents of the POX and SR reactions. The SR reaction absorbs part of the heat generated by the POX reaction, limiting the maximum temperature in the reactor. The net result can be a slightly exothermic process.

Autothermal reforming provides a fuel processor compromise that operates at a lower O/C and lower temperature than the POX; is smaller, quicker starting, and quicker responding than the SR, and results in high H_2 concentration.. A catalytic POX reaction must be used to reduce the temperature to a value compatible with the SR temperature.

Other Reforming Combinations: There have been fuel processor configurations where a non-catalytic POX is placed in series with a steam reformer. Without catalyst, the POX reaction must be at a higher temperature than the steam reformer reaction. These reactions must take place in separate compartments with heat exchange and a wall between them (18). This configuration is not considered within the definition of autothermal reforming.

State-of-the-Art Components

Developers have brought fuel processing technology to the point where conversion of all fuels of interest to fuel cells have been demonstrated to a degree. Natural gas steam reforming is used in commercial fuel cell units. There has been equal success with steam reforming light distillates, although these fuels are not commonly used. Tests have been performed on reactors and complete small fuel processors using methanol, gasoline, and diesel, all suitable for vehicle use. These tests have not advanced to operation over prolonged periods. However, there have been tests that indicate these fuels can be processed in POX and ATR reactors with high levels of sulfur. Water-gas shift and methods to lower CO even to a few ppm have been developed, but the final CO cleanup processes are in an early stage of development. All fuel processors need additional engineering development to reduce volume, weight, and cost to allow widespread fuel cell power unit use. The state-of-the-art information below is based primarily on U.S. or closely-related fuel cell programs.

State-of-the-Art Components - Conversion of Fuels

Generic Fuel Conversion: Considering the spectrum of fuel conversion from steam reforming to partial oxidation should convey a basic understanding of the reforming processes. An elegant, general equation published by the ANL describes fuel conversion throughout the spectrum. Autothermal reforming falls within this spectrum so that the equation encompasses processes of interest to fuel cells. The equation does not apply to complete combustion, but that conversion process is not relevant to fuel cells (20, 22, 23). The general, idealized equation is:

$$C_nH_mO_p + x(O_2 + 3.76N_2) + (2n - 2x - p)H_2O = nCO_2 + (2n - 2x - p + m/2)H_2 + 3.76xN_2 \quad (8\text{-}4)$$
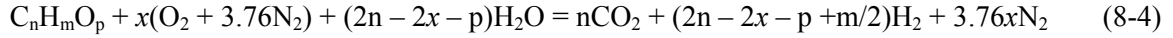
where x is the molar ratio of oxygen-to-fuel. This ratio is very important because it determines:

- The minimum amount of water that is required to completely convert the carbon in the fuel to carbon dioxide $(2n - 2x - p)$. Excess water is used in practice to ensure the conversion, resulting in water in the reformate (right side of the equation). Typically, one or two moles of water for every mole of oxygen are used.
- The maximum hydrogen yield $(2n - 2x - p + m/2)$
- The maximum concentration (percentage) of hydrogen in the reformate $\{[2n - 2x - p + m/2]/[n + (2n - 2x - p + m/2) + 3.76x]$ all times 100$\}$
- The heat of reaction $\{\Delta H_r = n(\Delta H_{f,CO_2}) - (2n - 2x - p)\Delta H_{f,H_2O} - \Delta H_{f,fuel}\}$.

Decreasing the oxygen-to-fuel ratio, x, results in increasing demand for water (water-to-fuel ratio), with commensurate increases in the yield and concentration of hydrogen in the reformate gas. When $x = 0$, the equation reduces to the strongly endothermic steam reforming reaction. The reaction becomes less endothermic with increasing oxygen. It becomes thermoneutral[48] at $x = x_0$ (0.44 for methane). Above this point, the reaction becomes increasingly exothermic. At $x = 1$ with methane, the pure POX reaction, the feed contains sufficient oxygen to convert all of the carbon in the fuel to CO_2. No water needs to be added. The equation is a mix of the steam reforming reaction and the POX reaction at values of x between 0 and n.

Beyond $x = [n - (p/2)] = n$ (when p = 0), where water is a product, the heat of reaction is determined by the phase of the product water. At still higher values, the excess oxygen oxidizes the hydrogen to produce water. Finally, at stoichiometric combustion, all carbon and hydrogen are converted to carbon dioxide and water. Here, $x = X_c = [n - (p/2) + (m/4)]$. The value of x reduces to 2 with CH_4 as the fuel.

Equation 8-4 depicts a total reaction where the fuel input is converted to carbon dioxide. Actually, the initial reforming step is carried out at elevated temperatures, where a mixture of carbon monoxide and carbon dioxide is formed. In the subsequent reformate conversion step, the carbon monoxide is converted via the water-gas shift to carbon dioxide:

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (8\text{-}5)$$

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48. The thermoneutral point (of oxygen-to-carbon ratio) is where the enthalpy of the reaction is zero, $(\Delta H_{f,298} = 0)$.

There may be additional, downstream inputs of water/steam and oxygen/air for water-gas shift and selective oxidation to further reduce CO, if needed.

When the function of a fuel processor is to convert a fuel to hydrogen, the fuel conversion efficiency is

$$\text{Efficiency} = \frac{\text{Lower Heating Value of Anode Fuel(s) Produced}}{\text{Lower Heating Value of Fuel Used}} \tag{8-6}$$

The fuel conversion efficiency for methane conversion to hydrogen is 93.9% at the thermoneutral point, $x = 0.44$ (an ATR reaction) and 91.7% at $x = 0$ (the SR reaction). The difference between the two efficiency values is exactly equivalent to the loss represented by the latent heat of vaporization of the H_2O that escapes with the combustions products in the SR burner exhaust. The concentration of hydrogen is 53.9% at $x = 0.44$ (ATR) and 80% at $x = 0$ (SR).

Equation 8-4 and related heats of reaction can be manipulated to show that the maximum efficiency is a state point function, regardless of path (steam reforming, partial oxidation, or autothermal reforming), and is achieved at the thermoneutral point. In practice, x is set slightly higher than the thermoneutral point so that additional heat is generated to offset heat losses from the reformer. Table 8-1 presents efficiencies at the thermoneutral point for various hydrocarbon fuels.

**Table 8-1 Calculated Thermoneutral Oxygen-to-Fuel Molar Ratios (x_o) and
Maximum Theoretical Efficiencies (at x_o) for Common Fuels (23)**

$C_nH_mO_p$	n	m	p	$\Delta H_{f,fuel}$ (kcal/gmol)	m/2n	X_o, $\Delta H_r = 0$	Efficiency (%)
Methanol $CH_3OH(l)$	1	4	1	-57.1	2	0.230	96.3
Methane CH_4	1	4	0	-17.9	2	0.443	93.9
Iso-Octane $C_8H_{18}(l)$	8	18	0	-62.0	1.125	2.947	91.2
Gasoline $C_{7.3}H_{14.8}O_{0.1}(l)$	7.3	14.8	0.1	-53.0	1.014	2.613	90.8

Because the components and design of a fuel processor depend on the fuel type, the following discussion is organized by the fuel being processed.

Hydrogen Processing: When hydrogen is supplied directly to the fuel cell, the fuel processing section is no more than a storage and delivery system. However, in general applications, hydrogen must be generated from other fuels and processed to meet the system requirements.

Natural Gas Processing: The major constituents of pipeline gas are methane, ethane, propane, CO_2, and, in some cases, N_2. Sulfur-containing odorants (mercaptans, disulfides, or commercial odorants) are added for leak detection. Because neither fuel cells nor commercial reformer

catalysts are sulfur tolerant, the sulfur must be removed. This is usually accomplished with a zinc oxide sulfur polisher and the possible use of a hydrodesulfurizer, if required. The zinc oxide polisher is able to remove the mercaptans and disulfides. However, some commercial odorants, such as Pennwalt's Pennodorant 1013 or 1063, contain THT (tetrahydrothiophene), more commonly known as thiophane, and require the addition of a hydrodesulfurizer before the zinc oxide sorbant bed. The hydrodesulfurizer will, in the presence of hydrogen, convert the thiophane into H_2S that is easily removed by the zinc oxide polisher. The required hydrogen is supplied by recycling a small amount of the natural gas reformed product. Although a zinc oxide reactor can operate over a wide range of temperatures, a minimum bed volume is achieved at temperatures of 350 to 400°C (660 to 750°F).

The CH_4 in the natural gas is usually converted to H_2 and CO in a SR reactor. Steam reforming reactors yield the highest percentage of hydrogen of any reformer type. The basic SR reactions for methane and a generic hydrocarbon are:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{8-7}$$
$$C_nH_m + nH_2O \leftrightarrow nCO + (m/2 + n) H_2 \tag{8-8}$$
$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{8-9}$$

In addition to natural gas, steam reformers can be used on light hydrocarbons such as butane and propane, and on naphtha with a special catalyst. Steam reforming reactions are highly endothermic and need a significant heat source. Often the residual fuel exiting the fuel cell is burned to supply this requirement. Fuels are typically reformed at temperatures of 760 to 980°C (1,400 to 1,800°F).

A typical steam reformed natural gas reformate is presented in Table 8-2.

Table 8-2 Typical Steam Reformed Natural Gas Reformate

| Mole Percent	Reformer Effluent	Shifted Reformate
H_2	46.3	52.9
CO	7.1	0.5
CO_2	6.4	13.1
CH_4	2.4	2.4
N_2	0.8	0.8
H_2O	37.0	30.4
Total	100.0	100.0

A POX reformer also can be used to convert gaseous fuels, but does not produce as much hydrogen as the steam reformers. For example, a methane-fed POX reformer would produce only about 75% of the hydrogen (after shifting) that was produced by an SR. Therefore, partial oxidation reformers are typically used only on liquid fuels that are not well suited for steam reformers. Partial oxidation reformers rank second after steam reformers with respect to their hydrogen yield. For illustration, the overall POX reaction (exothermic) for methane is

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad\qquad (8\text{-}10)$$

When natural gas fuels are used in a PAFC or a PEFC, the reformate must be water-gas shifted because of the high CO levels in the reformate gas. A PAFC stack can tolerate about 1% CO in the cell before having an adverse effect on cell performance due to catalyst poisoning. The allowable CO level in the fuel gas for a PEFC is considerably lower. The shift conversion is often performed in two or more stages when CO levels are high. A first high-temperature stage allows high reaction rates, while a low-temperature converter allows for a higher conversion. Excess steam is used to enhance the CO conversion. A single-stage shift reactor is capable of converting 80 to 95% of the CO (24). The water gas shift reaction is mildly exothermic, so multiple stage systems must have interstage heat exchangers. Feed temperatures of high- and low-temperature shift converters range from approximately 260 to 370°C (500 to 700°F) and 200 to 260°C (400 to 500°F), respectively. Hydrogen formation is enhanced by low temperature, but is unaffected by pressure.

When used in a PEFC, the reformate must pass through a preferential CO catalytic oxidizer, even after being shifted in a shift reactor. Typically, the PEFC can tolerate a CO level of only 50 ppm. Work is being performed to increase the CO tolerance level in PEFC.

At least two competing reactions can occur in the preferential catalytic oxidizer:

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \qquad\qquad (8\text{-}11)$$
$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad\qquad (8\text{-}12)$$
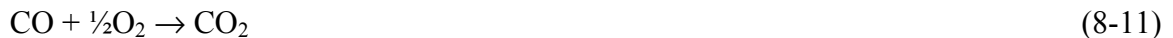
The selectivity of these competing reactions depends upon the catalyst and determines the quantity of required oxygen (25).

Liquid Fuel Processing: Liquid fuels such as distillate, naphtha, diesel oils, and heavy fuel oil can be reformed in partial oxidation reformers. All commercial POX reactors employ noncatalytic POX of the feed stream by oxygen in the presence of steam with reaction temperatures of approximately 1,300 to 1,500°C (2,370 to 2,730°F) (24). For illustration, the overall POX reaction for pentane is

$$C_5H_{12} + 5/2O_2 \rightarrow 5CO + 6H_2 \qquad\qquad (8\text{-}13)$$

The overall reaction is exothermic, and largely independent of pressure. The process is usually performed at 20 to 40 atmospheres to yield smaller equipment (24). A typical fuel composition for a fuel oil fed POX reformer is presented in Table 8-3. The CO contained in this reformate may need to be converted with a shift converter or selective catalytic converter, depending upon the specific fuel cell being fed.

Table 8-3 Typical Partial Oxidation Reformed Fuel Oil Reformate (24)

Mole Percent (dry, basis)	Reformer Effluent
H_2	48.0
CO	46.1
CO_2	4.3
CH_4	0.4
N_2	0.3
H_2S	0.9
Total	100.0

Alcohols are steam-reformed at lower temperatures (<600°C) while alkanes[49] and unsaturated hydrocarbons require slightly higher temperatures. Cyclic hydrocarbons and aromatics have also been reformed at relatively low temperatures, however a different mechanism appears to be responsible for their reforming. Blended fuels like gasoline and diesel, that are mixtures of a broad range of hydrocarbons, require temperatures of >700°C maximum hydrogen production. Methanol, one of the fuels being considered for transportation applications, can be converted into hydrogen by steam reforming:

$$CH_3OH = CO + 2H_2 \qquad\qquad (8\text{-}14)$$
$$CO + H_2O = CO_2 + H_2 \qquad\qquad (8\text{-}15)$$

The equivalent overall result of these two specific reactions is:

$$CH_3OH + H_2O = CO_2 + 3H_2 \qquad\qquad (8\text{-}16)$$

The optimum choice of operating conditions is close to a steam to methanol ratio of 1.5 and a temperature range of 250°C to 399°C. Pressure does not influence the reaction rate, but very high pressures limit the equilibrium conversion, which otherwise is better than 99% at the preferred range of 5 to 15 bars. The Cu/Zn/Al and Cu/Zn/Cr based catalysts have been used in industrial units for many years (17).

Coal Processing: The numerous coal gasification systems available today can be reasonably classified as one of three basic types: 1) moving-bed, 2) fluidized-bed, and 3) entrained-bed. All three of these types use steam and either air or oxygen to partially oxidize coal into a gas product. The moving-bed gasifiers produce a low temperature (425 to 650°C; 800 to 1,200°F) gas containing devolatilization products such as methane and ethane, and hydrocarbons including naphtha, tars, oils, and phenol. Entrained-bed gasifiers produce a gas product at high tempera-ture (>1,260°C; >2,300°F composed almost entirely of hydrogen, carbon monoxide, and carbon dioxide. The fluidized-bed gasifier product gas falls between these two other reactor types in composition and temperature (925 to 1,040°C; 1,700 to 1,900°F).

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49. Alkanes are saturated hydrocarbons, i.e., no double carbon bonds. Examples are CH_4, C_2H_6, C_3H_8, and $C(n)H(2n+2)$. Alkenes have carbon-carbon double bonds such as ethene C_2H_4 and $C(n)H(2n)$.

The heat required for gasification is supplied by the partial oxidation of coal. Overall, the gasification reactions are exothermic, so waste heat boilers often are used at the gasifier effluent. The temperature, and therefore composition, of the product gas depends upon the amount of oxidant and steam, as well as the design of the reactor.

Gasifiers typically produce contaminants that must be removed before entering the fuel cell anode. These contaminants include H_2S, COS, NH_3, HCN, particulates, tars, oils, and phenols. The contaminant levels depend on both the fuel composition and the gasifier employed. There are two families of cleanup that remove the sulfur impurities: hot and cold gas cleanup systems. Cold gas cleanup technology is commercial, has been proven over many years, and provides the system designer with several choices. Hot gas cleanup technology is still developmental and would likely need to be joined with low temperature cleanup systems to remove the non-sulfur impurities in a fuel cell system. For example, tars, oils, phenols, and ammonia could all be removed in a low temperature water quench followed by gas reheat.

A typical cold gas cleanup process following an entrained gasifier would include the following subprocesses: heat exchange (steam generation and regenerative heat exchange), particulate removal (cyclones and particulate scrubbers), COS hydrolysis reactor, ammonia scrubber, acid gas (H_2S) scrubbers (Sulfinol, SELEXOL), sulfur recovery (Claus and SCOT processes), and sulfur polishers (zinc oxide beds). All of these cleanup systems increase process complexity and cost, while decreasing efficiency and reliability. In addition, many of these systems have specific temperature requirements that necessitate the addition of heat exchangers or direct contact coolers.

For example, a COS hydrolysis reactor operates at about 180°C (350°F), the ammonia and acid scrubbers operate in the vicinity of 40°C (100°F), while the zinc oxide polisher operates at about 370°C (700°F). Thus, gasification systems with cold gas cleanup often become a maze of heat exchange and cleanup systems.

Typical compositions for several oxygen-blown coal gasification products are shown in Table 8-4.

Table 8-4 Typical Coal Gas Compositions for Selected Oxygen-Blown Gasifiers

Gasifier Type	Moving-Bed	Fluidized-Bed	Entrained-Bed			
Manufacturer	Lurgi (20)	Winkler	Destec	Koppers-Totzek	Texaco	Shell
Coal	Illinois No. 6	Texas Lignite	Appalachian Bit.	Illinois No. 6	Illinois No. 6	Illinois No. 6
Mole Percent						
Ar	trace	0.7	0.8	0.9	0.9	1.1
CH_4	3.3	4.6	0.6	-	0.1	-
C_2H_4	0.1	-	-	-	-	-
C_2H_6	0.2	-	-	-	-	-
CO	5.8	33.1	45.2	43.8	39.6	63.1
CO_2	11.8	15.5	8.0	4.6	10.8	1.5
COS	trace	-	-	0.1	-	0.1
H_2	16.1	28.3	33.9	21.1	30.3	26.7
H_2O	61.8	16.8	9.8	27.5	16.5	2.0
H_2S	0.5	0.2	0.9	1.1	1.0	1.3
N_2	0.1	0.6	0.6	0.9	0.7	4.1
NH_3+ HCN	0.3	0.1	0.2	-	-	-
Total	100.0	100.0	100.0	100.0	100.0	100.0

Reference Sources: (26, 27)
Note: All gasifier effluents are based on Illinois No. 6, except the Winkler, which is based on a Texas Lignite, and the Destec, which is based on an Appalachian Bituminous.

Other Solid Fuel Processing: Solid fuels other than coal can be utilized in fuel cell systems. For example, biomass and RDF (refuse-derived-fuels) can be integrated into a fuel cell system as long as the gas product is processed to meet the requirements of the fuel cell. The resulting systems would be very similar to the coal gas system with appropriate gasifying and cleanup systems. However, because biomass gas products can be very low in sulfur, the acid cleanup systems may simply consist of large sulfur polishers.

State-of-the-Art Components - Cleaning and Reformate Gas Alteration (Removal Of Contaminants): Besides their basic fuel reforming function, fuel processors require the removal of impurities that degrade the fuel processor or fuel cell performance. Sulfur is the major contaminant encountered. Carbon monoxide reduction for low temperature fuel cells and avoidance of carbon deposition are also addressed. A typical processing chain for a low temperature fuel cell will have a hydrodesulfurizer, a halogen guard, a zinc oxide sulfur absorber, a catalytic reformer, a high temperature shift converter, a second halogen guard, and low temperature shift converter. Figure 8-2 provides insight into how these may be arranged. The function of all these components, except the reformer, is to remove impurities. For the PEFC, an additional device is necessary to remove essentially all CO, such as a preferential oxidizer (28).

Sulfur Reduction: There are high temperature and low temperature methods to remove sulfur from a fuel reformate. Low temperature cleanup, such as hydrodesulfurizing (limited to fuels with boiling end points below 205°C), is less difficult and lower in cost so should be used where possible, certainly with low temperature fuel cells. Sulfur species in the fuel are converted to

H₂S, if necessary, then the H_2S is trapped on zinc oxide. A minimum bed volume of the zinc oxide reactor is achieved at temperatures of 350 to 400°C. Thermodynamic and economic analyses show that it is appropriate to use high temperature cleanup with high temperature fuel cells.

There is a vast difference between removing sulfur from a gaseous fuel and a liquid fuel. The sulfur in a liquid fuel is usually removed after it is converted to a gas. This by removing the sulfur in the reforming reactor at high temperature, or by incorporating sulfur resistant catalysts. Sulfur resistant catalysts are being developed, but none are mature enough for present use. ANL is developing catalysts to reform gasoline, and have demonstrated that their catalyst can tolerate sulfur. The ANL catalyst has been shown to tolerate (100s of hours) sulfur present in natural gas in an engineering scale reformer.

At least one developer has a liquid-phase fuel desulfurizer cartridge that will be used to remove sulfur prior to fuel vaporization. Other developers remove the sulfur immediately after vaporization and prior to reforming. Hydrogen must be recirculated to the removal device to convert the sulfur species to H_2S so that it can be entrapped on zinc oxide. Zinc oxide beds are limited to operation at temperatures below 430°C to minimize thermal cracking of hydrocarbons that can lead to coke formation. Thermodynamics also favor lower temperatures. At higher temperatures, the H_2S cannot be reduced to levels low enough for shift catalyst or to reach fuel cell limits. For sulfur removal in the reformer, the presence of significant concentrations of steam in the fuel gas has a negative impact on the reaction equilibrium, leading to a higher concentration of H_2S than could be achieved with a dry fuel gas.

Carbon Monoxide Reduction: The use of CO as a fuel in high temperature cells and water-gas shift reactions to lower carbon monoxide to conditions suitable for a PAFC or a PEFC have been previously described. Fuel gas reformate contains 0.5 to 1% by volume of CO even after the shift reactions. Present PEFCs operate below 100°C. At these temperatures, even small amounts of CO are preferentially adsorbed on the anode platinum (Pt) catalysts. This blocks access of H_2 to the surface of the catalyst, degrading cell performance (29). Reformate for PEFC stacks must contain very low (<50 ppm) CO to minimize Pt absorption to a reasonable value to maintain sufficient active sites for the oxidation of H_2. This can be achieved in two ways, by air injection into the anode at up to about 4% of the reformate feed rate or by reducing CO concentration prior to the cell: even at 50 ppm, catalyst poisoning by CO must be mitigated by the injection of some air at the anode. For the latter approach, a preferential oxidizer (PROX) is used to reduce CO concentration prior to the cell. It has highly dispersed supported Pt or Pt-Ru (ruthenium) catalyst. Such catalysts act on the principle of selective adsorption of CO onto the active Pt or Pt-Ru (relative to H_2), leading to CO being selectively oxidized by stoichiometric amounts of air co-fed to the catalyst bed. As the CO is oxidized, the gas temperature rises, which decreases the selectivity of CO adsorption on the catalyst and also increases the kinetics of the reverse water-gas shift reaction. In practice, the PROX process is carried out in stages to permit cooling between stages. The PROX is a relatively large unit that operates at 100 to 180°C (22). Preferential gas cleanup by selective oxidation results in 0.1 to 2% H_2 lost (30).

Carbon Deposition Avoidance: The processing of hydrocarbons always has the potential to form coke. Coke formation is influenced by the composition of the fuel, the catalyst, and the

process conditions (e.g., partial pressure of steam). Coke causes the greatest problems in gas flow paths and on catalyst. Carbon deposition not only represents a loss of carbon for the reaction, but more importantly also results in deactivation of the catalyst due to deposition at the active sites. Thermal cracking[50] in over-heated preheaters and manifolds can easily form carbon. If the fuel conversion reactor is not properly designed or operated, coking is likely to occur. Thermo dynamic equilibrium provides a first approximation of the potential for coke formation. Free carbon in hydrocarbon fuels forms according to the three equations, (8-1), (8-2), and (8-3). Figures 8-4 and 8-5 show the effect of increasing steam on carbon deposition for methane and octane, respectively. Increasing steam, hydrogen, and carbon dioxide concentrations alleviates carbon deposition. Low contents of aromatics and alkenes help to maintain the activity of the catalyst (10). No carbon deposits at low temperatures (~600°C) in mixtures containing at least two atoms of oxygen and four atoms of hydrogen per atom of carbon. At these conditions, all carbon is present as CO_2 or CH_4 (7).

Higher hydrocarbon fuels show a greater tendency for carbon formation than does methane. One method to alleviate carbon deposition problems in the fuel processor is to use special catalysts either containing alkali or based on an active magnesia support. With a highly active catalyst, the limit permitted on the final boiling point of the hydrocarbon feedstock is related mainly to the possibility of desulfurizing the feed to below 0.1 ppm, rather than to the reactivity of the hydrocarbons. With proper desulfurization, it has been possible to convert light oil into syngas with no trace of higher hydrocarbons in the reformate gas (17).

Coke formation resulting from higher hydrocarbon fuels can also be eliminated with an adiabatic pre-reformer. The adiabatic reformer is a simple fixed bed reactor. By adiabatic pre-reforming, all higher hydrocarbons are converted at low temperature (below ~500°C) with steam into methane, hydrogen, and carbon oxides at conditions where carbon formation does not occur. It is possible to use a high pre-heating temperature (650°C or above) for internal reforming in MCFC and SOFC without the risk of carbon formation. For natural gas containing only minor amounts of higher hydrocarbons, adiabatic pre-reforming at a steam to carbon ratio as low as 0.25 mole/atom has been demonstrated. For heavier feedstocks such as naphtha, operation at a steam to carbon ratio of 1.5 has been proven in industry. Pilot tests have been carried out at a steam to carbon ratio of 1.0 with reformate recycle.

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50. Thermal cracking is the breaking of a hydrocarbon carbon-carbon bond through the free-radical mechanism. Cracking may result in the formation of lower chained hydrocarbons, the original "cracked" hydrocarbon, or further cracking of the hydrocarbon to soot.

Figure 8-4 Carbon Deposition Mapping of Methane (CH$_4$)
(Carbon-Free Region to the Right of Curve)

Steam Reforming

Autothermal Reforming
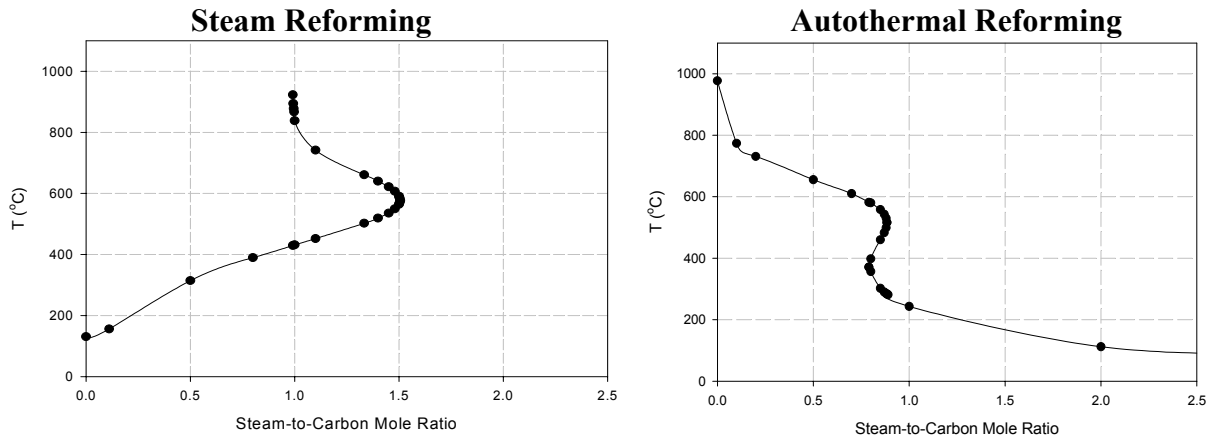
Figure 8-5 Carbon Deposition Mapping of Octane (C$_8$H$_{18}$)
(Carbon-Free Region to the Right and Above the Curve)

Steam Reforming
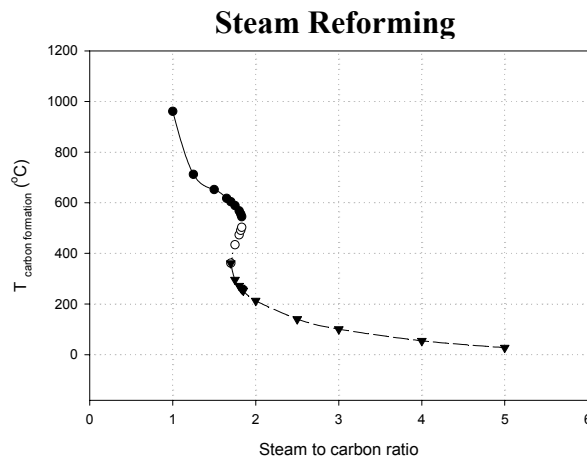
Coking can be also be avoided by operating at high temperatures and at high oxygen-to-carbon ratios, where the ratio is based on the total atoms of oxygen contained in the steam and air feeds. For a given O/C ratio in the feed, it is preferable that the oxygen comes from water. Thus, for a given O/C, SR is preferred over ATR, which is preferred over POX; "preferred" meaning that coke formation can be avoided while still operating at a lower temperature (20, 23, 31).

Other Impurities Reduction: Halides in fuels such as naphtha have deleterious effects on steam reforming and low temperature shift, thus halogen guards must be included in fuel processing.

There are many types of coal with different compositions, including harmful species. One common constituent, HCl, will cause formation of stable chlorides and corrosion in a MCFC. There has not been much work in SOFC yet on this topic. It is doubtful whether low temperature cells will be fueled by coal.

Research & Development Components

There are two major areas where fuel processor developers are focusing their research and development efforts, catalyst development and process/engineering development. A smaller, long term effort on novel processing schemes is in the early stages of investigation.

Catalyst Development. Performance targets for the fuel processor for transportation fuel cell systems will require that the reforming catalysts used in these processors exhibit a higher activity and better thermal and mechanical stability than reforming catalysts currently used in the production of H_2 for large-scale manufacturing processes. To meet these targets, reforming catalysts will have to process the feed at a space velocity of 200,000/hr (based on the volumetric flow of the feed in the gaseous state at 25°C and 1 atm) with a fuel conversion of >99% and a H_2 selectivity of >80% (moles of H_2 in product/moles of H_2 "extractable" from the feed), and have a lifetime of 5,000 hr. Given the potential market for transportation applications, many of the major catalyst producers, such as Johnson-Matthey, Engelhard Corporation, and dmc^2 division of OM Group, Inc., have begun to develop new reforming catalysts (32). An ANL program is focused on improving long-term stability (minimize deactivation), an important, immediate goal, reducing coke formation for higher hydrocarbons, and improving catalyst sulfur tolerance while addressing cost issues. A major issue is to demonstrate that the catalyst can operate for 40,000+ hours in stationary applications and 4,000+ hours in transportation applications. It is believed that no one has successfully demonstrated these targets. Another issue is that coke formation will be problematic with higher hydrocarbons, especially diesel. Most industrial reforming catalysts are operated steam-rich to minimize coke formation. However, this increases the size of the reformer as well as the energy needed to vaporize the water. This option may not be viable for reformers used with fuel cells. Finally, <20 ppb of S is the target for use with nickel steam reforming catalyst. Most fuels being considered contain either sulfur at the ppm level, such as gasoline, or added as an odorant for safety reasons, such as to natural gas. The ability of the catalyst to process fuels containing ppm levels of sulfur would be beneficial. The ANL catalysts are based on solid oxide fuel cell technology, where a transition metal is supported on an oxide- ion-conducting substrate, such as ceria, zirconia, or lanthanum gallate, that has been doped with a small amount of a non-reducible element, such as gadolinium, samarium, or zirconium. Platinum was the transition metal used in the first generation of the ANL catalyst. Because of concerns over the cost associated with using a precious metal-based catalyst, work has begun on reducing the cost of the catalyst either by replacing Pt with a less expensive non-noble metal or by using a combination of a noble metal, at a considerably lower metal loading, and with a base metal without sacrificing performance. Work is proceeding on catalysts based on Ni, Rh, and combinations of Ni and Rh. Süd-Chemie, Inc. currently produces reforming catalysts based on this technology under a licensing agreement with Argonne (32).

There is also a need to develop better water gas shift catalysts (7, 33, 34), especially catalysts that operate at temperatures ranging from 200-300 °C. Commercial shift catalysts based on FeCr and CuZn oxides are available, but are not designed for the rapid startups and frequent exposure to oxidizing conditions that will be experienced during normal operation of fuel processors developed for transportation applications. These commercial catalysts have fixed size, high density, and are susceptible to contaminant poisoning by ingredients found in infrastructure fuels. Of primary concern is the need to reduce these catalysts in a well-controlled manner that minimizes temperature rise in order to achieve maximum catalyst activity and to prevent the

exposure of the catalyst in the reduced state to oxidizing conditions. For example, the CuZn catalysts will sinter if exposed to >270 ^{o}C and are pyrophoric when exposed to air in the reduced state. Present commercial catalysts are developed for process plant service where transient conditions are not a concern. There is a need for highly active catalysts that can be supported on a low density monolith that do not require reduction in order to be active and are stable when exposed to oxidizing conditions. ANL is developing a more robust shift catalyst that will work better under transient operating conditions than present catalysts developed for process plant service. The advantage of this catalyst over standard catalysts is that it is air stable, which is needed for many start-up and shutdown cycles. There is a trade-off of a moderate reduction in activity (35).

There is also a need to demonstrate that the low-temperature, PROX catalysts have high selectivity toward CO and long term stability.

Process/Engineering Development Numerous engineering and process issues are being addressed by fuel processor developers (20, 31, 36). Several major issues are:

- As the size of the catalyst bed increases, the segregation within an ATR reactor bed toward over-oxidation and catalyst overheating in the front of the bed, and air starvation and carbon formation in the back end of the bed are important to consider. Maintaining a good temperature distribution in the bed, especially with a large reactor, is identified as one of the challenges facing this approach.
- Fuel processor tests have been on the order of 40 hours, although the fuel processors have been tested for 1,000 hours on natural gas. There is a need is to show similar results at realistic operating conditions and further engineering development to enhance the catalyst activity and make the fuel processor lighter and smaller.
- There is a need to investigate improved and simplified fuel processor designs. Examples are combining the reformer and the desulfurizer in a single stage to reduce weight and volume, producing an integrated vaporizer design, and designing for a wide variation of fuel vaporization temperatures to allow fuel flexible operation.
- Transient issues are important in transport applications and should be addressed early by testing. The challenge is to demonstrate the operation at high sulfur content over the full operating envelope of the vehicle – start-up, transients, shutdown, sulfur spikes in the fuel, etc. using the same processor.

Novel Processing Schemes: Various schemes have been proposed to separate the hydrogen-rich fuel in the reformate for cell use or to remove harmful species. At present, the separators are expensive, brittle, require large pressure differential, and are attacked by some hydrocarbons. There is a need to develop thinner, lower pressure drop, low cost membranes that can withstand separation from their support structure under changing thermal loads. Plasma reactors offer independence of reaction chemistry and optimum operating conditions that can be maintained over a wide range of feed rates and H_2 composition. These processors have no catalyst and are compact. However, results are preliminary and have only been tested at a laboratory scale.

Other: Although not R&D, it should prove beneficial for fuel cell developers to provide fuel tolerance specifications to fuel processor developers. Tolerances should be established by

standard definition, determination methods, and measurement procedures. This would aid the fuel processor developer to deliver products compatible with various fuel cell units. Of particular importance are sulfur and CO limits.

8.2   Power Conditioning

Power conditioning is an important enabling technology necessary for converting the DC electrical power generated by a fuel cell into usable AC power for stationary loads, automotive applications, and interfaces with electric utilities. Fuel cells are emerging as an attractive power source by virtue of their inherently clean, efficient, and reliable nature (37, 38). As the demand for various applications such as remote generation, backup power generation, distributed generation, and automotive applications increase, their prices are expected to decrease, thus furthering their penetration into the market (37). Further, unlike batteries, fuel cells can continuously provide power as long as reactants are supplied.

It should be noted that the electrical attributes of a fuel cell are far from an ideal electric power source. A typical fuel cell stack has a DC output voltage that varies widely (2:1) with the load current and age of the fuel cell, and has limited overload capability. Furthermore, a fuel cell stack is slow to respond to load changes (if the fuel supply is adjusted for best efficiency), needs considerable parasitic power for pumps and blowers, and may possibly be slow to start up due to heating requirements. Low cost power-conditioning units are essential for fuel cell systems to be cost competitive (39, 40, 41). Furthermore, the power conversion technology must create, as well as supply, the market demand in a cost effective manner for fuel cell technology to be viable. The aim of this section is to explore several possible power conversion approaches to interface a variety of fuel cell power sources for the following applications:
- Fuel cell power conversion for supplying a dedicated load in an isolated/remote location
- Fuel cell power conversion for supplying backup power (uninterrupted power supply) to a load connected to a local utility
- Fuel cell power conversion for supplying a load operating in parallel with the local utility (utility interactive)
- Fuel cell power conversion for connecting directly to the local utility
- Power conversion for automotive fuel cell applications
- Power conversion for a fuel cell turbine hybrid interfaced to local utility

Fundamentals of various power conversion stages such as DC-DC, DC-AC and AC-AC are essential for processing the electric energy generated by fuel cells. Section 8.2.1 is intended for those who need to understand the basics of power conversion building blocks. After examining basic power conversion blocks, Sections 8.2.2 to 8.2.8 delve into power conversion architectures suitable to serve a few kW to several MW power levels. Numerous power electronics books and scientific papers are available to provide additional details (42, 43, 44, 45).

8.2.1   Introduction to Fuel Cell Power Conditioning Systems
The purpose of this section is to provide an introduction to various power conversion blocks such as DC to DC, and DC to AC employed in fuel cell power conditioning systems. The section also includes a brief review of modern power semiconductor devices, gate drive requirements, packaging, and cooling methods. Figure 8-6 shows a block diagram of a fuel cell power plant.